Theoretical Research on Adsorption Properties of Tin Oxide to Gases Dissolved in Transformer Oil

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Abstract

H_2, CO, CH_4, C_2H_6, C_2H_4 and C_2H_2 are the typical fault characteristic gases dissolved in transformer oil. Based on the density function theory, SnO_2 surface model, gas molecular models and adsorption models were built, responsibility. A first principles calculation was performed and their adsorption properties were investigated in detail. The calculated adsorption energy ΔE_{ads} for CH_4, C_2H_4, C_2H_2, C_2H_6, H_2 andCO are 0.147eV, 0.253eV, 0.248eV, 0.219eV, 0.126eV, and 0.171eV. The calculated charge transfer between the gas molecule and adsorption SnO_2 surface for CH_4, C_2H_6, C_2H_4, C_2H_2, H_2 and CO is 0.56e, 0.51e, 0.48e, 0.22e, 0.06e and 0.11e, respectively.

Keywords

Adsorption properties, tin oxide, online monitoring, transformer oil.

1. Introduction

Power transformer is one of the most important apparatus in power transmission and its operation conditions directly affect the safety and reliability of the power system [1-2]. Once fault happened on power transformer, it will cause great damage to the national economy. At present, most of the large power transformers are still oil-immersed transformers, when the transformer internal paper-oil insulation fault occurs due to overheating or partial discharge, it may generate gaseous compounds such as H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4 and C_2H_2 and most of them are dissolved in transformer oil. On-line monitoring of these dissolved gases is one of the key technologies for power transformer conditional maintenance [3-4].

With the advantages simple manufacture technique, low cost, rapid response and recovery time, long life and stability, etc, semiconductor SnO_2 based gas sensor are the most promising sensing material. But the sensing mechanism is in controversial. An atomic level understanding of the sensing behavior of SnO_2 based gas sensor to those typical transformer fault characteristic gases is crucial.

2. The Calculation Method

Based on the framework of density function theory (DFT), the total energies and electronic structures of SnO_2, H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4 and C_2H_2, are calculated using Cambridge Sequential Total Energy Package (CASTEP) program in this paper [5-6]. Exchange-correlation function between electrons is described by the Revised- Perdew-Burke-Ernzerh (RPBE) form of Generalized Gradient Approximation (GGA). Interaction between nuclei and electrons is approximated with ultra-soft pseudo-potential to treat 2s and 2p electrons of O atom , 5s and 5p electrons of Sn atom, 1s electrons of H atom, 2s and 2p electrons of C as bands and valence electrons .The cutoff energy of the plane-wave is set at 380eV to ensure energy convergence within 1-2 meV/atom. The maximum root-mean-square convergent tolerance is 1.0x10-6 eV/atom. In the whole calculation process of geometry optimization and energy calculation all atoms were allowed to relax in all directions freely [7-8].

Orbital energy is investigated with DMol3 module, which based on the linear combination of atomic orbital (LCAO) theory. As the CASTEP module, we use the RPBE form of GGA to describe the exchange-correlation function. The orbital cutoff quality is set as 4.3Å and the maximum root-mean-square convergent tolerance is 1.0x10-6 eV/atom. The basis set is approximated with double numerical orbit base group and orbit polarization function to handle the p orbit polarization of hydrogen atom.

3. Results and Discussion

It is known to all that tin oxide is typical n-type sensing material, and typical fault characteristic gases dissolved in transformer oil like H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4 and C_2H_2 are reducing gases. As known to all that SnO_2 is a typical n-type semiconductor and its gas-sensing property was mainly controlled by the surface. When gas sensor was placed in certain concentration detection gas, gas molecule adsorbed on the surface firstly, and modified the resistance and conductance of the adsorption surface.

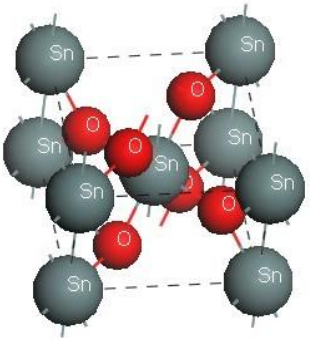

Fig. 1 The unit cell model of rutile SnO2

As we know that rutile SnO_2 crystal has four major low index surfaces (110), (101), (100) and (001), respectively [5-7]. In particular, the (110) surface is of the most thermodynamical stable surface, and it has been widely used to investigate the surface properties. Therefore we used the first properties calculation method to discuss the adsorption process of gas with SnO_2 (110) surface.

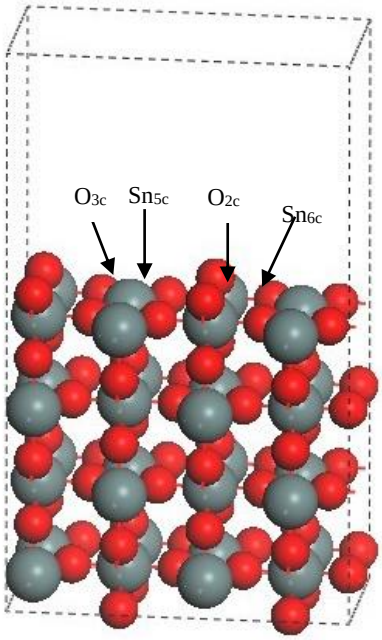

Fig. 2 The atomic model of SnO2 (110) surface

Firstly we built the rutile SnO_2 unit cell model as shown in Fig. 1 with lattice parameters a=4.737 Å and c=3.186 Å, where each Sn atom bonded with six O atoms nearby, and corresponding O with three

Sn. To preserve symmetry, the top and bottom layers of the slab were taken to be identical, and a surface vacuum slab of 10Å was added to the (110) surface normal to avid unwanted interaction between the slabs and its periodic images.

A super cell consisted a 1x1surface unit cell was employed, which was composed of a finite number of layers but of infinite extent. As shown in Fig. 2 the SnO_2 (110) surface as a single slab consisting of several atomic layers, which was cut from the optimized bulk structure. The central five layers were constrained at their sites, while the surface and subsurface layers on either side of the slab were allowed to relax freely for all the calculations. There are four kinds of surface atoms O_{2c}, O_{3c}, Sn_{5c}, Sn_{6c}, respectively, as shown in Fig. 2. The outermost atomic layer is composed of two-coordinate oxygen anions O_{2c}, which occupy bridging positions between tin fully coordinated tin atoms Sn_{6c} located in the second layer. Unsaturated five coordinated tin atoms Sn_{5c} and fully coordinated tin atoms Sn_{6c} as well as fully coordinated oxygen anions O_{3c} occupied in the second layer. And the third atomic layer is constituted of sub-bridging oxygen atoms. The molecule models of typical fault characteristic gases dissolved in transformer oil like H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4 and C_2H_2were shown in Fig. 3.

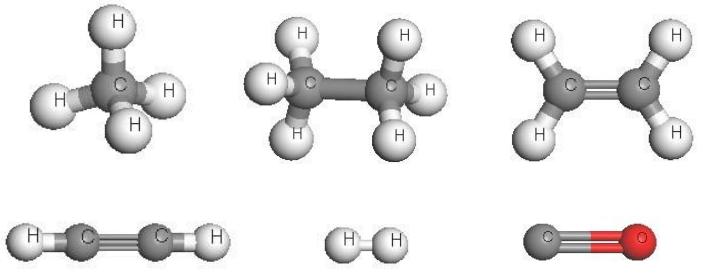

Fig. 3 The gas molecule models of fault gases

In this paper we mainly investigated various gas molecules adsorbed on O_{2c} bridging oxygen point of SnO_2 (110) surface. We calculated adsorption energy ΔE_{ads}, a key parameter in predicting the adhesive property of adsorption system. The adsorption energy is defined as the following equation [8]:

$$\Delta E_{ads} = E_{surf} + E_{gas} - E_{gas+surf} \quad (1)$$

Where E_{surf} is the energy of SnO_2 (110) surface before adsorption, E_{gas} is the energy of free gas molecule and $E_{gas+surf}$ is the total energy of the adsorption system with gas adsorbed. In general, a positive ΔE_{ads} indicates that the molecule adsorption process is exothermic and the adsorption system is energetically stable. For the purpose of comparison, all energies are calculated with the supercell in identical size.

Table 1 Adsorption energy on SnO2 (110) surface

gas	ΔE_{ads}/eV
methane	0.147
ethylene	0.253
acetylene	0.248
ethane	0.219
hydrogen	0.126
carbon monoxide	0.171

The calculated adsorption energies for power transformer fault gases adsorbed on SnO_2 (110) surface are represented in Table 1. According to the definition of adsorption energy, a positive value

demonstrates an exothermic reaction, which means a stable adsorption process. The bigger the adsorption energy is, the greater the excitation chance of the gas molecule electrons. In our calculation results, the ΔE_{ads} for methane, ethylene, acetylene, ethane, hydrogen and carbon monoxide are 0.147eV, 0.253eV, 0.248eV, 0.219eV, 0.126eV, and 0.171eV. It can be considered as the strong interaction between ethylene gas molecule and bridging oxygen as the ΔE_{ads} of ethylene is the biggest, that is to say more opportunity of ethylene gas molecule self-adsorbed on SnO_2 (110) surface.

We further investigated the Mulliken population and charge transfer between the gas molecule and adsorption surface to perform the sensing mechanism of the rutile tin oxide. The total number of electrons reduces at different levels after adsorbed on the surface. The lost electron number for CH_4, C_2H_6, C_2H_4, C_2H_2, H_2 and CO is 0.56e, 0.51e, 0.48e, 0.22e, 0.06e and 0.11e, respectively. Accordingly the lost electrons from adsorbed gas molecule are received by the (110) surface. It will decrease the height of barrier in the depletion region, increase the conductance of the sensor and result in an increase in output voltage.

It should be noted that it is controversial to quantitatively interpret the gas-sensing properties, due to possible deviations between experimental conditions and ideal theoretical models. However, a qualitative comparison in the same adsorption system should be reliable.

4. Conclusion

In this study, based on the density function theory a first principles calculation was performed to understand the sensing properties of SnO_2 based sensor to various fault characteristic gases extracted from power transformer oil. The calculated adsorption energy and charge transfer between gas and SnO_2 surface provides a qualitative explanation to the sensing properties of SnO_2 based sensor to various fault characteristic gases extracted from power transformer oil.

References

[1] H. Xiong, C. X. Sun, and R. J. Liao. Study on kernel-based possibilistic clustering and dissolved gas analysis for fault diagnosis of power transformer[J], Proceedings of the CSEE, Vol. 25 (2005) No.2, p.162-166.

[2] L. J. Zhou, G. N. Wu, and P. Tang. The model of semiconductor gas sensor for on-line monitoring in insulating oil[J], Power System and Automation, Vol. 30 (2006) No.10, p.75-78.

[3] W. G. Chen, Y. X. Yun, and C. Pan. Analysis of infrared absorption properties of dissolved gases in transformer oi[J], Proceedings of the CSEE, Vol. 28 (2008) No.16, p.148-153.

[4] I. Villar, U. Viscarret, I. Etxeberria-Otadui, and A. Rufer. Global loss evaluation methods for nonsinusoidally fed medium-frequency power transformers[J], IEEE Transactions on Industrial Electronics, Vol. 56 (2009) No.10, p.4132-4140.

[5] F. Ciriaco, L. Cassidei, M. Cacciatore, and G. Petrella. First principle study of processes modifying the conductivity of substoichiometric SnO_2 based materials upon adsorption of CO from atmosphere[J], Chemical Physics, Vol. 303 (2004) No.1, p.55-61.

[6] M. Mäki-Jaskari, T. T. Rantala, and V. V. Golovanov. Computational study of charge accumulation at SnO_2 (110) surface[J], Surface Science, Vol. 577 (2005) No.2, p.127-138.

[7] Y. Xue, and Z. Tang. Density functional study of the interaction of CO with undoped and Pd doped SnO_2 (1 1 0) surface[J], Sensors and Actuators B: Chemical, Vol. 138 (2009) No.1, p.108-112.

[8] W. Zeng, T. M. Liu, D. J. Liu, and E. J. Han. Hydrogen sensing and mechanism of M-doped SnO_2 (M= Cr^{3+}, Cu^{2+} and Pd^{2+}) nanocomposite[J], Sensors and Actuators B: Chemical, Vol. 160 (2011) No.1, p.455-462.